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THE ELECTRON SPIN RESONANCE SPECTRA OF THE MONONEGATIVE IONS OF o-, m-, AND p-TERPHENYL

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It is well known that negative ions of conjugated hydrocarbons are produced by contact reduction with alkali metals in solution[1,2], and a number of the electron spin resonance spectra of the mononegative ions made by use of this method are observed[3]. The spectrum of the mononegative ion of para-terphenyl (p-diphenylbenzene) which was obtained by the aforementioned way was also observed by De Boer and Weissman[4], but it was not analyzed in detail. We have measured the ESR spectra of the mononegative ion radicals of *p*-terphenyl and its isomers *m*- and *o*- terphenyl which are produced by the reduction with the mirror of sodium and of potassium, respectively, the solvents of these hydrocarbons in each case being either purified and degassed tetrahydrofuran (THF) or dimethoxyethane (DME). Some of the ESR spectra of the terphenyl radicals are shown in the figures 1 to 3. From these figures it becomes clear that there is an influence of solvent on the ESR spectra, although we have not found so much difference between (a) and (b) in Fig. 1. In the spectra of these hydrocarbons the effect of alkali metals, Na or K, has not observed in spite of change of temperature and concentration of samples. It will be noted that, for example, in DME solvent the spectrum of dilute *o*-terphenyl anion may be described in terms of about 200 lines (Fig. 3, (a)), but hyperfine lines in the case of THF solvent do not split into more than 35 lines even in very dilute solution (Fig. 3, (b)), and the latter spectrum is almost equal to that of much concentrated *o*-terphenyl in DME. When measured at low temperature, -15°C to -30°C, the ESR spectrum of *m*-terphenyl mononegative ion in THF was

Table 1. Line widths of the spectra of *o*-, *m*-, and *p*-, terphenyl anion radicals

Treated	Terphenyl		
	o-	*m*-	*p*-
with Na in THF	0.26	0.16	0.11
with K in THF	0.34	0.16	0.11
with Na in DME	0.06	0.08	0.05
with K in DME	0.06	0.07	0.05

1) D. E. Paul, D. Lipkin and S. I. Weissman: *J. Amer. Chem. Soc.* 78 116 (1956)
2) P. Balk, G. T. Hoijtink and J. W. H. Scheurs: *Rec. Trav. Chim.* 76 813 (1957)
3) D. J. E. Ingram "*Free Radicals as Studied by the Electron Spin Resonance*" Butterworths, 1958
4) E. De Boer and S. I. Weissman: *J. Amer. Chem. Soc.* 80 4549 (1958)

Table 2 Hyperfine coupling constants of *o*-, *m*-, and *p*-terphenyl anion radicals

Coupling constants	Terphenyl		
	o-	*m*-	*p*-
a_2*	/	/	1.20
a_2'	1.76	1.37	1.61
a_3'	0.49	0.31	0.46
a_4'	3.02	2.35	2.47
a_5	2.28	/	/
a_6	0.61	5.08	/

* Suffix indicates the ring position.

very similar to that of the same ion in DME obtained at room temperature. The results are summarized in Table 1 and 2. Table 1 shows that the line widths of the spectra measured in DME are 2 to 6 times smaller than those of the spectra measured in THF, and metal ions do not affect the line widths so much. From these results we may conclude that there is an influence of solvent on the hyperfine lines of the ESR spectra of the mononegative ions. In order to clarify the mechanism of spin-lattice relaxation in which the solvent, especially its structure, takes a part, a further investigation is under way.

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